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Atomic structure of the α-Ga(001) surface investigated by scanning tunneling microscopy: Direct evidence for the existence of Ga_2 molecules in solid gallium

O. Züger and U. Dürig*
IBM Research Division, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland
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The (001) surface of α-Ga single-crystal surfaces was investigated with the scanning tunneling microscope (STM) under ultra-high-vacuum conditions. The sputter-cleaned surface exhibits large, atomically flat terraces extending over distances of several 1000 Å. On the atomic scale, STM images reveal a 1×1 reconstruction of the surface lattice. The measured step height between the (001) terraces provides direct evidence for the existence of molecular Ga_2 dimers, a long-standing assumption that previously lacked clear experimental confirmation.

Gallium is a trivalent metal with an unusual crystal structure in the stable low-pressure phase, called α-Ga. The structure is commonly described in terms of a face-centered orthorhombic unit cell with eight atoms per cell[1] [Fig. 1(a)]. A peculiar feature is that each atom has only one nearest neighbor at a distance of 2.4 Å. The six next-nearest-neighbor atoms are within a shell with a radius between 2.71 and 2.80 Å. Nearest-neighbor atom pairs are located within (100) planes and are centered at the lattice sites of the unit cell. The pairs are alternatingly tilted by $\pm 16.9°$ with respect to the [001] axis. Apart from α-Ga, at least eight other phases with different structures are known at high pressure or low temperature.[2]

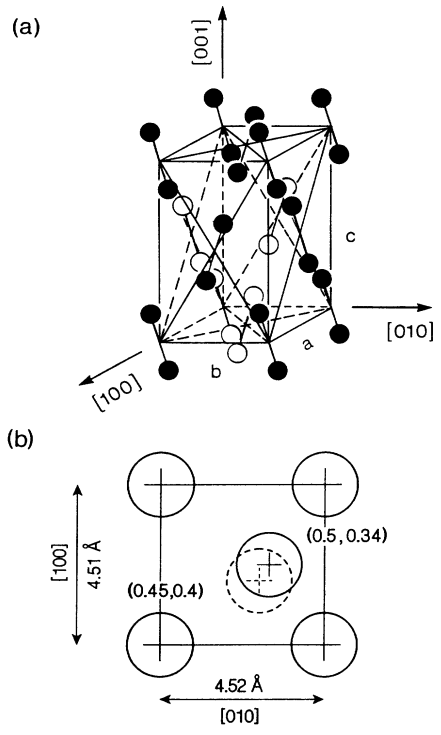

FIG. 1. (a) Face-centered orthorhombic unit cell of α-Ga. The length of the axes are $a=4.51$ Å, $b=4.52$ Å, $c=7.64$ Å. Each site of the cell is occupied by one nearest-neighbor atom pair. (b) Truncated bulk structure of the Ga(001) surface (solid circles) and the reconstruction (dashed circle) as observed by STM. Note that the mirror symmetry along the [010] axis is broken as a result of the reconstruction.

The distance between nearest-neighbor atom pairs is comparatively short for a normal metallic bond. This has led to speculations about the covalent nature of this bond. Thus, α-Ga would be a rare example of an elemental metallic molecular crystal (the metallic high-pressure phase of iodine being the other example known to date[3]). Several physical properties further substantiate this conjecture. The thermal and electrical conductivities are highly anisotropic, being lowest along [001], which is close to the direction of the presumed Ga_2 dimers.[4] In liquid Ga, however, these conductivities are about a factor of 2 higher than the corresponding values along the [001] axis of the crystal. Similar behavior is found in most semimetals (Sb, Bi, Te) and especially in semiconductors (Si, Ge), whose constituents are unequivocally covalently bonded.[5]

Gallium has an unusually low melting temperature of 29.78 °C and the density in the liquid state is higher than in the crystalline state: the corresponding change in specific volume is about 3.2%.[5] The latter property is common in solids that consist of molecular units, again in agreement with the postulated molecular character of α-Ga.

Further indication of the covalent character arises from measurements of electronic properties. Optical reflectivity spectra measured on evaporated Ga films contain a sharp absorption peak at a photon energy of 2.3 eV.[6] In a photoemission experiment on polycrystalline Ga, the density-of-states curves derived from the photo electron yield spectra showed a broad maximum at an energy $E=E_F-1.2$ eV and an unusually steep decrease towards E_F.[7] Both features were assigned to the covalent bond in α-Ga.

Theoretical evidence for the covalent character of α-Ga was first provided by band-structure calculations based on pseudopotential approximations.[8,9] Occupied and unoccupied Σ bands along the [001] direction are remarkably flat and symmetric about E_F. Recently, an *ab initio* study based on local density approximation was performed to elucidate the phase diagram of the different lattice struc-

tures and their electronic properties.[10] The authors found that among the different phases of Ga the molecular structure of α-Ga is the state of lowest energy at normal pressure. The electronic density of states extracted from the band structure has two pronounced peaks above and below E_F, reflecting the bonding and antibonding state of the Ga_2 molecule. The absorption peak observed in optical spectra[6] is well confirmed by this calculation.

For the investigation of the atomic structure of α-Ga (henceforth denoted as Ga) with a scanning tunneling microscope (STM), the (001) surface is well suited because the postulated Ga_2 dimers are oriented almost perpendicular to the surface. In principle, the (001) surface can be formed in two ways: by cutting the crystal either at a plane that intersects the dimer bonds or at a plane that separates the dimer layers. If molecular Ga_2 dimers constitute the lattice building units, the (001) must be of the latter type. Hence, the smallest step height is $c/2 \simeq 3.8$ Å. On the other hand, when both types of surfaces are simultaneously realized—which in turn would contradict the notion of covalently bonded Ga atoms pairs—steps with a height of $c/4 \simeq 1.9$ Å are present.

Ga(001) samples were cut from single crystals grown from the supercooled melt. The (001) surface, which has the highest packing density of all orientations, is faceting spontaneously on these crystals, which renders proper orientation of the samples easy. The (001) surface was polished with diamond paste down to a grain size of 0.25 μm. Then the samples were mounted on a sample holder and transferred into the ultrahigh vacuum chamber through an air-lock system. Several sputter-cleaning cycles with 2 keV Ne^+ ions at a sample temperature close to 0 °C were initially required to remove the native oxide layer. Once a clean surface had been obtained, three minutes of sputtering at room temperature prior to measurements was sufficient to assure cleanness of the surface. The final oxide contamination as checked by Auger electron spectroscopy was $< 0.3\%$ of a monolayer, increasing to $\simeq 1\%$ within 24 h. After preparation the samples were transferred to an STM designed specifically to perform experiments on Ga single-crystal surfaces up to the bulk melting point.[11]

The structure of the truncated bulk (001) surface can be described by an almost square lattice, 4.51×4.52 Å^2 along the [100] and [010] axes, respectively, with a two-atomic basis [Fig. 1(b)]. The corresponding basis coordinates in lattice units are (0,0) and (0.5,0.34). However, it turned out that the surface is reconstructed—as evidenced by low-energy electron diffraction. Sharp spots were observed in a fourfold symmetric pattern incompatible with the mirror symmetry expected from the truncated bulk model.

The nature of the reconstruction is unveiled in high-resolution STM images. An example is shown in Fig. 2. It was measured using an Ir tip and tunneling parameters $I_t = 1$ nA and $V_t = -0.3$ V (a negative V_t means tunneling out of occupied sample states). The actual corrugation amplitude, $\simeq 0.2$ Å$_{pp}$, is too small to be displayed directly owing to excessive $1/f$ noise originating from fluctuations of the tunneling gap.[11] To overcome this problem, the tip was modulated laterally by about 0.5 Å at a frequency of $\simeq 5$ kHz simultaneously while scanning, and the amplitude $\partial \ln I/\partial x$ of the induced tunnel current modulation was detected by means of a lock-in amplifier.[12] Assuming a constant tunneling barrier ϕ, the $\partial \ln I/\partial x$ signal—actually displayed in the figure—essentially represents the local gradient $\partial z/\partial x$ of the surface.

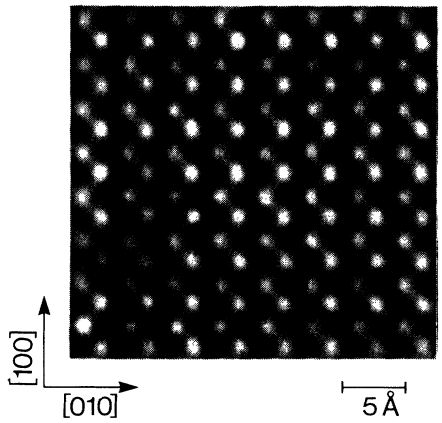

FIG. 2. Atomically resolved STM image (45×34 Å^2) of the Ga(001) surface, displaying the measured $\partial \ln I/\partial x$ signal (which essentially corresponds to $\partial z/\partial x$). The corrugation calculated from this signal is $\simeq 0.2$ Å$_{pp}$.

Close inspection of the STM image reveals a 1×1 reconstruction. The atom inside the unit cell is shifted by $\simeq 0.35$ Å from the expected position (0.5, 0.34) to the position (0.45, 0.40) [in lattice units, see Fig. 1(b)]. This shift of the atomic position can easily be seen from an angled view along the [010] direction. In addition, by resorting to lattice averaging techniques, we found that the topographic height of the corner atoms and that of the atom within the unit cell differ by $\simeq 0.05$ Å.

Henceforth, we shall concentrate on characterizing the surface structure on a larger scale. A typical STM image (10000×8000 Å^2) of the sputter-cleaned (001) surface is shown in Fig. 3. The gradient image $\partial z/\partial x$ calculated from individual line scans is displayed to enhance the visibility of the steps. The surface consists of remarkably large (001) terraces extending over several 1000 Å and separated by irregularly oriented step lines. The presence of such large, atomically flat areas is surprising, because the surface was sputter cleaned with 2 keV Ne^+ ions prior to the tunneling experiment. Surface defects (vacancies, adatom clusters) induced by the sputter-cleaning process are completely absent. Post-sputtering annealing of defects by surface diffusion would be one explanation for their absence: however, surface diffusion was never observed in STM images measured up to the onset of bulk melting.[13] Hence, removal of Ga from the (001) surface during sputter cleaning is most likely a layer-by-layer process involving ion-impact assisted kinetic processes leading to interlayer annealing of the surface.[14]

Further information about the structure of Ga is extracted from an analysis of the step height. The step-height distribution was obtained by convoluting the STM line scans with a step function whose width was larger than that of the steps in the line scans. The result was a

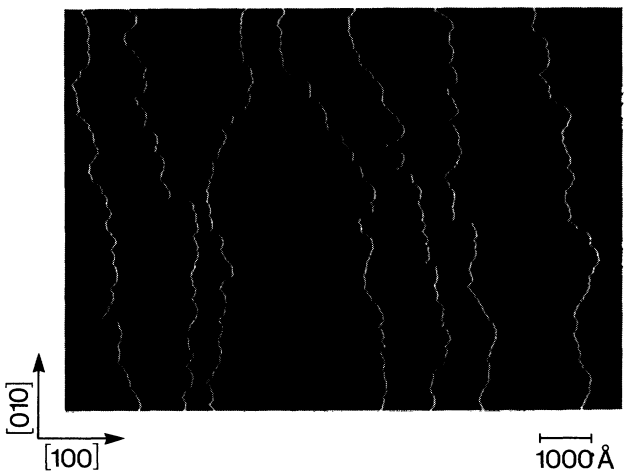

FIG. 3. Large-scale image (10000×8000 Å^2) of the (001) surface. The step edges are enhanced by displaying the calculated derivative $\partial z/\partial x$. The step height is 3.8 Å, as expected for single layers of Ga_2 dimers.

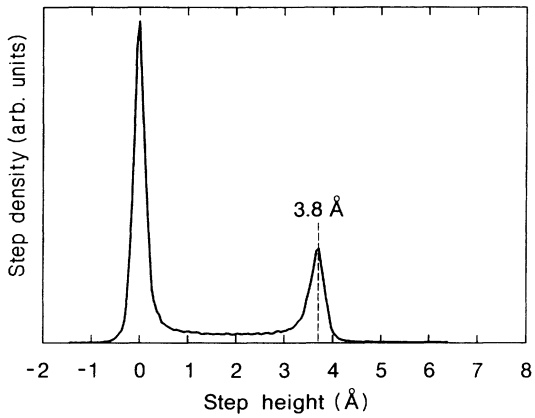

FIG. 4. Histogram of the step-height distribution measured on Ga(001) surfaces. The peak at zero height results from atomically flat terraces. The peak at 3.8 Å originates from steps that are formed by layers of Ga_2 dimers. There is no indication for the existence of steps with a height of 1.9 Å, which would originate from single-atom layers.

line scan with zero height on flat terraces, but with a narrow plateau around the position of the step. The height of this plateau corresponds to the height of the step (note that this operation corresponds to a discrete differentiation combined with an averaging over the width of the step function). Thus, a histogram of the height distribution of the transformed image represents the step-height distribution of the original image. Such a histogram is shown in Fig. 4. It was obtained from an image similar to Fig. 3, but with a slightly higher step density in order to improve statistics.

In Fig. 4, the main peak at zero height represents the flat terraces. The only other peak corresponds to steps with a height of 3.8 Å. The width of the peaks ($\simeq$0.2 Å) reflects height fluctuations of the measured topography due to noise. There is no indication of even a slight bump at 1.9 Å. Hence, we conclude that no layers consisting of single atoms are formed at the surface. This provides convincing evidence that Ga_2 dimers are indeed the basic building units of the crystal.

In conclusion, STM investigations of the (001) surface of α-Ga shows that large atomically flat terraces are formed by sputter cleaning the surface with Ne ions. A slight 1×1 reconstruction of the surface unit cell was discovered, which breaks the mirror symmetry along the [010] axis. An analysis of the step-height distribution reveals that no monoatomic steps are formed. This observation clearly shows that Ga_2 dimers are the basic constituents of the crystal. To our knowledge, no other technique has been able to confirm the postulated molecular structure of Ga with similar evidence so far.

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*Corresponding author, bitnet address: DRG at ZURLVM1.

[1]R. W. G. Wyckoff, *Crystal Structures,* 2nd ed. (Wiley, New York, 1962), Vol. I, p. 22. A word of caution is in order: of the six possible ways to assign *a*, *b*, *c* to the three crystal axes, at least three different versions can be found in the literature.

[2]See, e.g., Pierre de la Bretèque, *Gallium, Bulletin d'Information et de Bibliographie* (Alusuisse-France S. A., Marseille, 1970), Vol. 8; *Gallium,* 8th ed., Gmelins Handbuch der anorganischen Chemie, Vol. 36 (Verlag Chemie, Berlin, 1936), and references therein.

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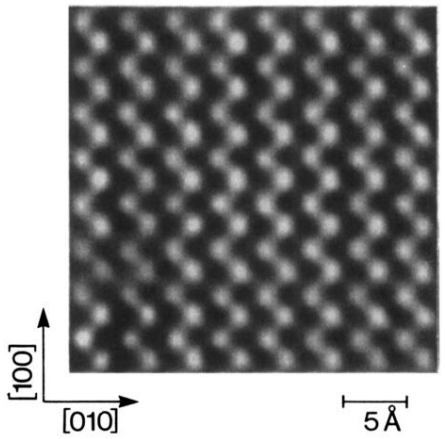

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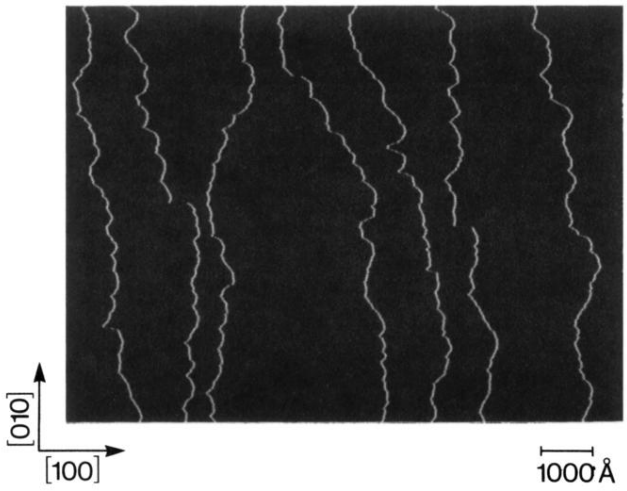

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